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BY

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NOTES ON THE DETERMINATION OF MOLYBDENUM[1]

By H. A. Doerner[2]

The Rare and Precious Metals Station of the U. S. Bureau of Mines has investigated several cases in which widely divergent amounts of molybdenum were reported by a number of custom laboratories to which quartered portions of the same sample had been sent for analysis.

On an oxidized lead ore containing considerable vanadium and a little molybdenum, the amount of the latter reported ranged from 3.14 to 0.24 per cent MoO_3. The high results were due to the fact that vanadium was estimated with, and reported as, molybdenum. When analyzed by the method described in this paper, 0.15 per cent MoO_3 was found, which is a fair agreement with the lowest figure previously reported.

In another and more unusual example, a fine-grained rock containing considerable graphite was submitted for analysis. As a white residue could not be obtained by treating this material with acid, several chemists decomposed the ore by a prolonged fusion with soda ash and nitre and leached the melt with hot water in order to insure the dissolution of any and all the molybdenum present. After precipitating and filtering the silica from the solution, acetic acid, ammonium acetate, and lead acetate were added to precipitate lead molybdate. The solution contained phosphorous derived from the ore, which precipitated as lead phosphate. The latter was mistaken for, and reported as, molybdenum. As two different chemists used essentially the same procedure, their results, although incorrect, checked. Other chemists using different methods found no molybdenum.

From these and other instances it is evident that reputable and conscientious assayers may make serious errors in determining molybdenum, and even duplication of results by different chemists does not necessarily insure against error.

The elements most likely to cause trouble are vanadium, tungsten, uranium, arsenic, antimony, titanium, tin, phosphorous, and chromium. The precautions necessary to eliminate these and other impurities vary with the type of ore and the method of analysis. Most texts present methods of limited application and omit or fail to emphasize adequately such precautions. No one method can be given that will best fit every case, but the following procedure has been selected as being the simplest reliable method for such occasional determinations of molybdenum in an ore as are encountered in customs work.

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[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6335."

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Qualitative Determination

If there is doubt concerning the presence of molybdenum in a sample, much time may be saved by making a preliminary qualitative test, as follows:

Fuse about 1 gram of the pulverized sample with several grams of soda ash and sodium peroxide in a nickel or iron crucible. Digest the melt in hot water, add H_2O_2, boil 10 minutes, and filter. Acidify the filtrate with HCl, and boil off the CO_2. An alkali thiocyanate is then added, immediately followed by zinc. If Mo is present a bright cherry-red color will appear and finally fade as the reduction by zinc proceeds. H_2O_2 will destroy the color, but when the peroxide has been reduced by nascent hydrogen the color reappears. Iron, nitric acid, and chloric acid will produce color which may be mistaken as an indication of molybdenum, but the reactions with zinc and H_2O_2 do not produce the same changes as when molybdenum is present.

If properly carried out as described, the above procedure is a delicate and reliable test for molybdenum. The depth of color produced will give an indication of the amount of molybdenum present.

Quantitative Determination

If the material is high-grade, weigh a half-gram sample; for low grade ore or tailings, take as much as 5 grams. Treat the finely pulverized sample with 40 c. c. of nitric acid and 7 c. c. of strong sulphuric acid. Digest one-half hour just below the boiling point, then heat to copious fumes. If any dark particles of ore remain, digest with more nitric acid and a gram of sodium chlorate, and again heat to fumes. Cool, add 50 c. c. of water and heat to dissolve soluble sulphates. Cool, filter, and wash with cold dilute sulphuric acid (1:20).

Unless the residue is perfectly white it should be tested by the qualitative method previously described. In the very rare cases where an appreciable amount of molybdenum remains in the residue, a more elaborate procedure than is given in this paper should be employed.

Most ores contain sufficient iron to combine with and precipitate all the arsenic present. If the filtrate from the insoluble residue contains but little iron, add 0.5 gram of ferric sulphate. Nearly neutralize the solution with ammonia, heat and pour it slowly into 75 c. c. of boiling hot, 15 per cent, ammonia water. If much lime is present, add 1 gram of sodium bicarbonate. Filter and wash twice with hot water. Wash the precipitate out of the paper and digest it 15 minutes with dilute ammonia. Again filter and wash well with hot water.

Add 5 grams of tartaric acid to the combined filtrates, warm, and saturate with hydrogen sulphide. If copper or other insoluble sulphides appear, they should be filtered off. The molybdenum remains in solution as thiomolybdate, which imparts a cherry-red color to the solution. A slight excess of dilute sulphuric acid is next added, which precipitates molybdenum trisulphide, leaving vanadium and tungsten in solution. After heating a short time to coagulate, the precipitate is filtered and washed with hydrogen sulphide water containing a little sulphuric acid.

To be certain that molybdenum is completely precipitated, it is necessary to add nitric and sulphuric acids to the filtrate, evaporate to fumes, cool, add more nitric acid, and again fume to insure destruction of organic matter. Cool, add sufficient water to dissolve the salts, add ammonia, tartaric acid, and hydrogen sulphide, and precipitate the molybdenum as before. This precautionary procedure is seldom necessary in commercial work.

The molybdenum trisulphide is dissolved in hot dilute aqua regia, and the solution is neutralized with ammonia. Add 7 c. c. of strong hydrochloric acid and 10 grams ammonium acetate. Dilute to 300 c. c., heat to boiling, and add slowly from a burette a solution of lead acetate until a test drop gives no color change with a drop of freshly-made tannic acid solution. Add a little more lead acetate, heat half an hour, and filter off the lead molybdate, washing with a 2 per cent solution of ammonium acetate.

The washed filter is placed in a fire-clay annealing cup and ignited at red heat in a muffle. After cooling, the ignited precipitate can be brushed out of the annealing cup onto a balance pan and weighed directly. The weight of $PbMoO_4$ times 0.2615 gives the weight of Mo in the precipitate.

If a large number of determinations is to be made, a standard solution of lead acetate may be employed to estimate the molybdenum volumetrically. Tannic acid is used as an outside indicator, the titration being simply the reverse of the common molybdate method of determining lead. A few titrations should be checked by weighing the precipitate of lead molybdate.

On many ores the filtrate from the iron precipitation may be acidified with acetic acid and titrated directly, but this procedure gives accurate results only when interfering elements are absent, and it is not a reliable method for an ore of unknown composition.

For a more complete discussion of this and other methods for estimating molybdenum, the reader is referred to U. S. Bureau of Mines Bulletin 212, "Analytical Methods for Certain Metals." This bulletin may be found in the larger technical libraries, or may be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C., by remitting the price of 40 cents directly to that official.